Photochemical UV/TiO_2 treatment of olive mill wastewater (OMW)

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Abstract

Olive mill wastewater (OMW) was treated by photocatalysis using TiO_2 under UV irradiation on the laboratory scale. The chemical oxygen demand, the coloration at 330 nm, and the level of phenols all showed decreases which, after a 24-h treatment, reached 22%, 57% and 94%, respectively. The differences between these three values indicate the persistence of colourless, non-phenolic compounds. Application of the novel Fictitious Atomic-Group Separation method showed an increase in carbon oxidation state and confirmed that the attack primarily concerns, aromatic moieties. A fine spectroscopic study revealed the occurrence of three successive phases during the degradation process, thought to correspond to three different categories of molecules in the OMW and the presence of pectin compounds.

Keywords: Olive mill wastewater; UV/TiO_2; Fictitious atomic-group separation; UV–visible spectroscopy; IRTF Spectroscopy

1. Introduction

The production of olive oil in the Mediterranean countries accounts for approximately 95% of the world production. It generates around 30 million m^3 of wastewater a year (Chamkha et al., 2001; Tabet et al., 2006). According to some reports, the chemical oxygen demand and biological oxygen demand (COD and BOD) values of these wastewaters are 200–400 times higher than those of typical municipal sewage. The very high levels of organic matter are mainly due to phenols, polyphenols, pectins, colloids, lipids and simple aromatic compounds resulting from olive cell wall degradation during oil extraction (Al Mallah et al., 2000; Centi et al., 2000; Chamkha et al., 2001).

To overcome these environmental problems, several biochemical techniques (ultrafiltration, coagulation, evaporation, etc.) have been tried (Fountoulakis et al., 2002) but owing to their high cost, few have ever been applied on an industrial scale. Other propositions involve the use of microorganisms for anaerobic (Ramos Cormenzana et al., 1995) or aerobic digestion (Dias Albino et al., 2004). Composting seems to be one of the most advantageous processes because it eliminates potentially dangerous residues and the final product can be used to improve soil quality.

Photocatalytic processes (Ollis and Al Ekabi, 1993) may be an alternative method. Heterogeneous photocatalysis, involving photoinduced redox reactions at the surface of semiconductor minerals, is a promising technique for the treatment of water contaminated by organic molecules (Hoffmann et al., 1995; Selli et al., 1999). Among the semiconductors available, titanium dioxide, or titania, is the

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most widely used in due to its outstanding stability (Frank and Bard, 1977).

The mechanism of photocatalysis by UV/TiO_2 has been described by several authors: Selli et al. (1999), Tanaka et al. (1999), Lanzalunga and Bietti (2000), Machado et al. (2000) and Chang et al. (2004), who have studied the degradation of various wastes, in particular lignin.

This paper reports the photocatalytic (UV/TiO_2) degradation of olive mill wastewater (OMW) as studied by elemental analysis, specially using the novel method of Fictitious Atomic-Group Separation (Tardy et al., 2005) and UV–visible and Fourier transform IR spectroscopy.

2. Methods

2.1. Origin and physical–chemical characteristics of OMW

The wastewater was taken from a modern three-phase centrifugation olive mill in Marrakech, Morocco. The main characteristics of the raw effluent were: electrical conductivity (EC) (44.3 ± 0.2 mS/cm) and pH (4.80 ± 0.01), which were measured at ambient temperature following the recommendations of Rodier (1971). The dry matter content (168.9 ± 7.4 g/L) was measured by drying at 105 °C for 24 h. Ashes (39.0 g/L) were determined by weighing after ignition at 550 °C for 24 h. The organic matter (129.9 ± 6.7 g/L) was obtained by difference. Total phenols (970 ± 9 mg/L) were extracted using ethyl acetate in the presence of phosphoric acid and ammonium sulphate (Macheix et al., 1990), and were assayed using Folin–Ciocalteu reagent. The chemical oxygen demand (COD) (135 ± 4 g/L) was determined using potassium dichromate, as described by Rodier (1987).

2.2. TiO_2/UV treatment

OMW was diluted to 1/100 and filtered through a 0.45 μm glass fibre filter. The photocatalyst was TiO_2 Degussa P25. It was added at a level of 1 g/L. The reactor had a working volume of 100 cm^3. The reactor was composed of a water-cooled double-walled Pyrex glass tube. The reaction mixture was continuously homogenized by magnetic stirring. It was illuminated by a vertical UV tube TLAD Philips 415W/05 (300–450 nm with an emission maximum at 365 nm). During the reaction, the suspension was maintained under constant oxygen bubbling. The medium was mixed in the dark during half an hour prior to irradiation to allow adsorption of the OMW organic matter onto TiO_2 particles. Samples were collected at −0.5 and 0 h before irradiation and at 4, 8, 16 and 24 h during irradiation. They were filtered using 0.45 μm Millipore filters to eliminate excess TiO_2 prior to analysis.

2.3. Elemental analysis (CHON)

The instruments used for C, H and N were a Fison Carlo Erba EA 1110, and a Carlo Erba 1106 for O. About 1 mg (0.8–1.2 mg) of the sample in a capsule made of tin (assay of C, H and N) or of silver (for assaying oxygen) was burned at 920–1000 °C. The quantity of each element is expressed in percent mass. Each determination was performed in duplicate. The raw results of the elemental analysis are expressed in weight % of C, H, O and N in the test aliquot. The sum of the four percentages gives the overall percentage of organic components. The difference from 100 gives the mineral fraction (ash).

In order to examine just the organic fraction and allow comparisons of the quality to be made, the total level of organic matter was expressed as 100% and the percentages of the four elements C, H, O and N were recalculated. Then, the molar formula was calculated by dividing the percentages by the atomic weight of the corresponding element. The rough overall formula, $C_xH_yO_zN_w$, was then obtained, and firstly gives the ratios between the different atoms. Then the Fictitious Atomic-Group Separation (FAS) method described by Tardy et al. (2000, 2005) and Ndira (2006) can be applied. As this technique is relatively recent, some instruction could prove useful.

1. Multiply the overall rough formula with a factor determined in such a manner that the value of N in the formula equals 1.
2. As N is essentially present in the form of peptide linkages (-CH(R)-CO-NH-CH(R')-), remove an –NH group. The overall formula can then be written CmHnOp, in which Cm represents "C total".
3. Calculate the maximum possible number of CH_2O groups (fictitious, of course), which give "C hydrated". What remains is available C and, according to the sample studied, H or O, one excluding the other.
4. Determine the number of CH_2 groups (again fictitious) which correspond to "C reduced" or CO groups which correspond to "C oxidized".
5. Generally there is some remaining C, which can be referred to as "C dry" or "C free".
6. Now establish the ratios of the fictitious functional groups between each other and with "C total".
7. Finally calculate the oxidation state of the carbon C^x by using either of the formulae:

$$C^x = 2CO/Ctotal \quad \text{or} \quad C^x = 2CH_2/Ctotal$$

in which CO is + and CH_2 is −.

CH_2O/Ctotal is the C hydration index while Cfree/Ctotal and Cfree/CH_2O are the indexes of C dehydration and polymerisation, and C^x is an index of C oxidation or reduction of (Tardy et al., 2000, 2005).

2.4. Ultraviolet–visible spectroscopy

The UV–visible spectra of treated OMW were recorded on an Ultraviolet SP 1800 spectrophotometer between 300 and 700 nm. The E_4/E_6 ratio (absorbance at 465/absorbance at 665 nm) was determined for each sample (Chen et al., 1977).

2.5. Fourier transform infrared spectroscopy (FTIR)

Potassium bromide pellets of each sample were prepared by pressing, under vacuum, a mixture of 250 mg of dried KBr and 1 mg of dialyzed and lyophilized sample. The spectra were obtained using a FTIR Perkin–Elmer 1600 spectrophotometer over a range of 4000–400 cm^{-1}, at a rate of 16 nm/s. They were recorded in absorbance to allow a valid comparison of the ratios of the absorbance peaks.

3. Results and discussion

3.1. Variation of the physical–chemical characteristics of OMW (Table 1)

The pH rose slightly after the addition of TiO_2 into the OMW solution, following adsorption of the organic matter onto titania particles. A small pH decrease was observed between 8 and 24 h of irradiation (about 0.5 pH unit). It can be explained by formation of acidic functions through oxidation. The electrical conductivity decreased during the 0.5-h dark step due to the adsorption of ions onto TiO_2 (causing the rise in pH), then it slightly increased after 8 h of irradiation, which could indicate progressive mineralisation and release of mineral ions, which formed salts. COD and total phenols decreased during the 0.5 h stirring step in the dark by 11% and 33%, respectively. It can be explained by adsorption of the organic matter onto TiO_2. During the illuminated phase, COD fell from 1.3 g/L to 1.05 g/L showing that mineralisation occurred. After 24 h of irradiation, mineralisation reached 22%. The drop in total phenols was much greater reaching about 96% after 24 h. The value 10.40 mg/L at 4 h of UV/TiO_2 is probably due to the formation of intermediates during the oxidation of polyaromatic compounds.

This is in good agreement with the interpretation of the TiO_2 OMW attack reported by da Silva Perez et al. (1998) and Machado et al. (2000) for various compounds: preferential attack of the electron-rich aromatic and olefinic groups, and attack at a lower rate of aliphatic side chains and carbohydrates.

3.2. Elemental analysis (CHON)

The elemental composition of OMW at various stages of treatment is presented in Table 2. The percentage of carbon, hydrogen and nitrogen decreased, while that of oxygen increased. This supports the notion of degradation by oxidation described above. The percentage of ash shows an overall slight increase, but irregularities of the phenomenon occurred and are most likely due to the OMW heterogeneity, probably at the molecular level.

Under the action of TiO_2 alone, the C/N ratio increased, indicating a strong fall in the nitrogen level, which likely corresponds to the hydrolysis of the protein component. It continued to increase, but less rapidly, under UV for up to 8 h then decreased. This means parallel oxidation of C at increasing levels. The O/C ratio increased regularly with time, clearly showing oxidation by TiO_2 alone then by the association UV/TiO_2. Both C/N and O/C ratios confirm that there is a direct action by TiO_2, which is amplified under UV irradiation. The C/H ratio was more or less stable throughout the treatment, indicating that even after 24 h of UV irradiation, there was little change in the structure of the undegraded molecules.

The fictitious atomic-group separation method (FAS) was applied to the above data. The results are presented in Table 3.

The ratio CH_2O/Ctotal rose sharply under the action of TiO_2 alone but there was then only a very slight increase between 0 and 4 h of TiO_2 plus UV and the slight fluctuations above 4 h were very close to stability. The state of hydration of C increased during the brief period of TiO_2 alone but remained practically stable thereafter.

The ratios Cfree/Ctotal and Cfree/CH_2O showed the same general pattern and, as CH_2O/Ctotal did not vary much, the variations of the first two ratios can be attributed to Cfree. The presence of TiO_2 alone therefore caused a decrease of Cfree, which continued steadily except for the 8 h point. This means that the attack, initially strong and then slowing down, particularly involves the aromatic structures represented by the group – Cfree. This is in agreement with the findings of da Silva Perez et al. (1998).

The oxidation state of carbon C^x increased during photocatalysis, confirming the oxidizing effect of the treatment, which here affected structures still present as macromolecules.

3.3. Ultraviolet–visible spectroscopy

The plots present the same overall pattern showing similarity between the chemical structures before and after treatment, and no UV-absorbent structures appear during treatment.

Table 1
Physical–chemical characteristics of OMW during the treatment

	Dark step		Irradiation step			
	−0.5 h	0 h	4 h UV	8 h UV	16 h UV	24 h UV
pH	4.62	4.91	4.91	4.92	4.75	4.43
EC (μS/cm)	839	822.5	820	820.5	832	847
COD (g/L)	1.35	1.20	1.30	1.20	1.15	1.05
Total phenols (mg/L)	8.13	5.45	10.40	8.53	0.48	0.46

Table 2
Elemental composition of the OMW at the different stages of treatment

	Percent weight						Atomic ratio		
	C	H	O	N	CHON	Ash	C/N	C/H	O/C
−0.5 h	37.01 ± 0.08	4.79 ± 0.04	33.44 ± 0.19	1.59 ± 0.01	76.83	23.17	27.15	0.64	0.68
0 h	34.47 ± 0.27	4.88 ± 0.02	35.74 ± 0.39	1.06 ± 0.08	76.15	23.85	37.82	0.59	0.78
4 h UV	33.86 ± 0.11	4.79 ± 0.01	38.32 ± 0.29	1.04 ± 0.05	78.01	21.99	38.04	0.59	0.85
8 h UV	34.06 ± 0.11	4.57 ± 0.03	35.73 ± 0.44	0.93 ± 0.01	75.29	24.71	42.65	0.62	0.79
16 h UV	32.54 ± 0.19	4.39 ± 0.02	38.85 ± 0.20	1.18 ± 0.03	76.96	23.04	32.19	0.62	0.90
24 h UV	31.52 ± 0.02	4.04 ± 0.01	39.00 ± 0.33	0.94 ± 0.01	75.5	24.5	39.31	0.65	0.93

Table 3
Ratios between fictitious chemical groups and oxidation states of C versus the duration of treatment

	−0.5 h	0 h	4 h UV	8 h UV	16 h UV	24 h UV
CH_2O/Ctotal	0.68	0.78	0.83	0.79	0.79	0.75
Cfree/Ctotal	0.25	0.17	0.15	0.21	0.10	0.07
Cfree/CH_2O	0.37	0.22	0.18	0.27	0.13	0.09
C^x	−0.15	−0.11	0.04	0.00	0.22	0.36

Similar results were reported by El Hajjouji et al. (2007) for OMW treated by aerobic biodegradation.

During the treatment, there was a decrease in absorption over the whole range of wavelengths studied, from 700 to 300 nm. Moreover, at the stages −0.5, 0 and 4 h of irradiation, the spectra presented a shoulder, between 350 and 400 nm, which then disappeared progressively.

This has also been reported by El Hajjouji et al. (2007). Machado et al. (2000) stated that the wavelength range required for lignin degradation is generally of lower energy (between 300 and 400 nm) than for phenols (<300 nm). This is due to the functional character of lignin with certain groups sensitizing the degradation of the phenolic units (Castellan et al., 1990). Lignin, largely present in pulp mill effluent, is a natural polymer whose main structural units consist of phenolic compounds (Tanaka et al., 1999). Lignin degradation in the presence of TiO_2 and UV light is due to the combined action of hydroxyl and superoxide radicals, the main reactive species generated in such a photocatalytic process in the presence of oxygen (Machado et al., 2000).

To study the absorbance variation, it was necessary to use a wavelength outside the area of influence of the shoulder. We chose to make the readings at $\lambda = 330$ nm, where measurements can be made with greatest accuracy. The plots show that absorbance decreases under the effect of the treatment, slightly during the first 8 h then a little faster. After 24 h of irradiation, absorbance dropped by 57%, corresponding to the disappearance of the same % of coloured constituents. This can be considered with respect to the drop in COD reported above, which only reached 22% after 24 h (see Section 3.1). The difference between the two decreases could be due to two factors:

(a) The formation of small colourless organic molecules which, at least temporarily, remain in the solution, for instance ethanol, glycerol and simple sugars which can be considered as degradation intermediates.
(b) The persistence, for varying periods of time, of only slightly coloured or colourless macromolecules relatively resistant to the UV/TiO_2 attack, and hence likely to be carbohydrates, suggesting that they are pectins.

The regression of absorbance versus time is a straight line with $R^2 = 0.99$. It can therefore be assumed that the whole disappearance process of coloured OMW components is linear with time, and hence that extrapolation is possible beyond the duration of the actual experiment.

With the equation: $y = -0.0487x + 2.1345$
a value of $y = 0$ was reached for $x = 43.82$, i.e. total degradation of the coloured components after 44 h of treatment.

The E_4/E_6 ratio (absorbance at 465 nm/absorbance at 665 nm) (Table 4) increased during treatment rising, from 6.01 at the initial stage to 7.09 after 24 h irradiation. It increases with decreasing molecular weight and condensation and can serve as an index of humification (Stevenson, 1982). Thus, a high ratio reflects a low degree of aromatic condensation (Stevenson, 1982). In a rather exhaustive study Chen et al. (1977) concluded that E_4/E_6 ratios of humic and fulvic acids were governed primarily by particle sizes and weights; secondary relationships were observed between the ratio and total acidity, the –COOH content and C and O contents. The slow increase of the E_4/E_6 ratio would then correspond to both a steady decrease of aro-

Table 4
E_4/E_6 ratio (absorbance at 465/absorbance at 665 nm) for treated OMW

	−0.5 h	0 h	4 h UV	8 h UV	16 h UV	24 h UV
E_4/E_6	6.01	6.36	5.12	5.19	8.42	7.09

Table 5
Absorbance bands from the IR spectra of treated OMW

Wavelength	Assignments
3400 cm^{-1}	–OH (phenols, alcohols and carboxylic groups)
2925 cm^{-1}	C–H stretching in aliphatic structures (fatty acids, waxes and other long-chain structures)
1716–1740 cm^{-1}	C=O stretching in carboxyls, acids and ketones
1620–1660 cm^{-1}	C=O stretching in amides I
	C=O stretching in ketones, acids and/or quinones
	C=C stretching in aromatics
1635 cm^{-1}	C=C conjugates or aromatics
1450–1460 cm^{-1}	C–H stretching in aliphatic structures
1400–1390 cm^{-1}	OH deformation and C–O stretching in phenolic OH, C–H deformation of CH_2 and CH_3 groups, COO– antisymmetric stretching
900–1300 cm^{-1}	C–H stretching and OH deformation in carboxyls, C–O of ethers on an aromatic ring and the N–H of amides II
<1000 cm^{-1}	Stretching of aromatic ethers, polysaccharides (C–H stretching)

matic condensation and an increase in the proportion of acid groups, i.e. to the attack of aromatic structures.

3.4. Fourier transform infrared spectroscopy (FTIR)

The interpretation is based on works of Tanaka et al. (1999), Ouatmane et al. (2000), Hafidi et al. (2005), El Hajjouji et al. (2007), and Smidt and Meissl (2006). The attribution of the absorption bands is summarized in Table 5.

First impressions suggest a strong resemblance between the IR spectra of all the samples, irrespective of the duration of photocatalysis, which suggests a high level of similarity between large non-dialyzable molecules during treatment. However, a closer study, based on the ratios between the intensities of the peaks (measured in OD units) is presented in Table 6 and brings out some interesting differences. All the ratios /3440 cm^{-1} underwent a clear decrease from 0 to 4 h, then increased until 16 h to fall again between 16 and 24 h indicating opposing relative variations in the level of –OH groups.

Considering the overall decrease of Cfree/Ctotal (linked to aromatic compounds), the stability of CH_2O/Ctotal (linked to carbohydrates) and the patterns presented by the /3440 curves (Table 6), attack must occur first on the aromatic parts of the non-dialysing macromolecules, paralleled by much less severe attack of the hydroxyl moieties and maybe by intermediate hydroxylation reactions. Here again, the observations are in agreement with the mechanism proposed by the authors cited above.

But, in any case, the process does not occur in a regular manner. The FAS curves (Table 3) and the curves of the /3440 ratios (Table 6) show irregularities which lead to a distinction being made between at least three successive phases: 0–4, 4–16 and 16–24 h during which the proportions of –OH successively rise, then fall then rise again. It can also be noted that in the UV linear regression plot, the points at 8 and 16 h lie above the curve, indicating attack that is slower than average, while 4 and 24 h are below, corresponding to faster attack. As the treatment actually received was perfectly constant, the existence of the three consecutive phases can only be accounted for by the occurrence of at least three different types of molecules in the OMW. This could correspond to three different combinations between the aromatic and pectin structures. The aromatic structures, more easily degraded by UV/TiO_2 are responsible for the black colour of the OMW and, in the initial effluent, certain resemblance with humic substances. The pectins, which are colourless or almost colourless, are responsible for the resistance to treatment.

Table 6
Ratios of IR absorption intensity (OD) of various peaks to absorption intensity at 3440 cm^{-1} versus irradiation time

	−0.5 h	0 h	4 h UV	8 h UV	16 h UV	24 h UV
619/3440	0.65	0.74	0.55	0.60	0.74	0.45
1076/3440	0.96	0.88	0.71	0.85	0.87	0.69
1400/3440	0.74	0.78	0.61	0.70	0.77	0.54
1635/3440	0.85	0.85	0.73	0.80	0.87	0.71
1733/3440	0.78	0.76	0.57	0.68	0.80	0.71
2925/3440	0.60	0.72	0.54	0.57	0.68	0.50

4. Conclusion

Treatment with UV/TiO_2 for 24 h primarily led to the disappearance of the great majority (94%) of the phenolic compounds – i.e. the compounds targeted by the technique. In addition, considering the mode of attack, the remaining 6% detected by Folin's reagent, are probably located at the surface of macromolecular structures and hence cause much less toxicity and/or pollution.

Also, the treatment degraded 57% of the coloured molecules and 22% of the compounds responsible for the chemical oxygen demand (COD), which appear to be mainly pectins.

The fine study of the results indicates the occurrence of three phases, which likely correspond to the presence of three categories of organic molecules, differing by their sensitivity to oxidation by the UV/TiO_2 system.

Olive mill wastewater has often been considered to be closely related to humic compounds because it is dark coloured, contains phenols and shares some of the properties of humic compounds. However, further studies of this effluent should pay greater heed to the presence of a high proportion of pectins.

Acknowledgements

This work was financially supported in part by an Eiffel grant from the French government. We thank S. Halladja, from the Université Blaise Pascal, Aubière, France, for her kind assistance in this work.

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